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Title: Composition for a curable aqueous coating

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Applicant: Dainippon Ink & Chemicals Inc.

1. Title of the invention:

Composition for a curable aqueous coating

2. What is claimed is:

A curable aqueous coating composition comprising as an essential component:

(A) a polymer aqueous dispersion prepared by an emulsion polymerization in the absence of a surface active agent, and

(B) an isocyanate series compound or a polymer thereof,

wherein in the presence of an aqueous copolymer prepared by copolymerizing in water at least 5 weight % of a crosslinkable functional group-containing water soluble ethylenically unsaturated monomer (a-1), at least 20 weight % of a water soluble ethylenically unsaturated monomer (a-2) having no above functional group, 0 to 75 weight % of a water insoluble ethylenically unsaturated monomer (a-3) and 0 to 40 weight % of an organic thiol compound (a-4) represented by Formula (I):



in which R represents a hydrocarbon group of C<sub>2</sub> to C<sub>36</sub> or a carboxylic acid residue and n represents an integer of 1 to 8, based on the whole amount of the monomers (a-1), (a-2), (a-3) and (a-4), in a proportion of 0.5 to 50

weight parts per 100 weight parts of the following whole ethylenically unsaturated monomers, the above polymer aqueous dispersion (A) is prepared by emulsion copolymerizing 5 to 50 weight % of the above ethylenically unsaturated monomer (a-1), 95 to 5 weight % of the above ethylenically unsaturated monomer (a-3) and/or the above ethylenically unsaturated monomer (a-2).

### 3. Detailed description of the invention

The present invention relates to a novel and useful curable aqueous coating composition, more specifically to a curable dispersed-in-water type coating composition obtained by emulsion polymerizing ethylenically unsaturated monomers including a crosslinkable unsaturated monomer in the presence of a specific water soluble curable type copolymer used as a polymer emulsion dispersant, that is, comprising a polymer aqueous dispersion and an isocyanate series compound or a polymer thereof as the essential components, the coating composition enabling to provide a cured coating film which is notably improved in a physical property of the coating film, a water resistance, a corrosion resistance and a chemical resistance. The composition has a excellent coating operation and is effective for preventing an aerial pollution since no organic solvent is contained in the volatile matters. It can be used at a room temperature or in forcible drying.

There has so far widely been used an aqueous paint prepared a solvent type thermosetting polymer as one means for preventing an environmental pollution such as an aerial pollution. However, it is originally

unsatisfactory as a high performance paint and has several defects.

In such the water dispersion type paint conventionally used, there can be given the problems that a coating film formed has an inferior gloss, that a water proof, a corrosion resistance and a weather resistance are not necessarily sufficient because of a surface active agent remained in the coating film and that a coating operation is inferior due to bubbling caused by the surface active agent.

In addition, when formaldehyde is used in forming such thermosetting coating film, a toxicity problem by released formaldehyde is included.

Further, in recent years, the requirement for energy saving is grown and there is requested a performance for curing a coating film not only by a low temperature baking but also by forcible drying and furthermore ordinary temperature drying.

An object of the present invention is to provide a curable coating composition in which no surface active agent is used for the purpose of solving the above problems.

That is, the present invention is to provide a curable aqueous coating composition comprising a polymer aqueous dispersion (A) and an isocyanate series compound or a polymer thereof (B) as an essential component, wherein in the presence of an aqueous copolymer prepared by copolymerizing in water at least 5 weight % of a crosslinkable functional group-containing water soluble ethylenically unsaturated monomer (a-1), at least 20 weight % of a water soluble ethylenically unsaturated

monomer (a-2) having no above functional group, 0 to 75 weight % of a water insoluble ethylenically unsaturated monomer (a-3) and 0 to 40 weight % of an organic thiol compound (a-4) represented by Formula (I):



in which R represents a hydrocarbon group of C<sub>2</sub> to C<sub>36</sub> or a carboxylic acid residue and n represents an integer of 1 to 8, based on the whole amount of the monomers (a-1), (a-2), (a-3) and (a-4), in a proportion of 0.5 to 50 weight parts per 100 weight parts of the following whole ethylenically unsaturated monomers, the above polymer aqueous dispersion (A) is prepared by emulsion copolymerizing 5 to 50 weight % of the above ethylenically unsaturated monomer (a-1), 95 to 5 weight % of the above ethylenically unsaturated monomer (a-3) and/or the above ethylenically unsaturated monomer (a-2).

There are available as the typical examples of the above crosslinkable functional group-containing water soluble ethylenically unsaturated monomer (a-1), a hydroxy group-containing monomer such as hydroxyalkyl ester of  $\alpha,\beta$ -unsaturated acid including hydroxyethyl metacrylate; an amide group-containing monomer such as amides of  $\alpha,\beta$ -unsaturated acid including metacrylamide, or various derivatives of amides of  $\alpha,\beta$ -unsaturated acid including N-alkoxymethyl acrylamide; and a glycidyl group-containing monomer such as glycidyl metacrylate.

The ethylenically unsaturated monomer (a-1) used is present in an amount of at least 5 weight %, preferably 10 weight % or more in the above aqueous copolymer.

The above water soluble ethylenically unsaturated monomer (a-2) having no crosslinkable functional group includes all water soluble ethylenically unsaturated monomers excluding the above various functional group-containing water soluble ethylenically unsaturated monomers. Of them, there can be given as the particularly representative examples thereof, a monomer having a sulfonic acid group and salts thereof such as vinyl toluenesulfonic acid and vinyl sulfonic acid; a carboxyl group-containing monomer and salts thereof such as unsaturated monobasic acid including metacrylic acid and crotonic acid or unsaturated dibasic acid including maleic acid and fumaric acid; monovinylpyridines such as vinylpyridine and 2-methyl-5-vinylpyridine; amino group-containing esters capable of forming salts of metacrylic acids, such as 2-dimethylaminoethyl metacrylate,  $\beta$ -(t-butylamino)ethyl metacrylate, and trimethylammonium 2-hydroxy-3-metacryloxypropyl; alkylamino group-containing vinyl ethers such as 2-dimethylaminovinyl ether; and alkylamino group-containing metacrylamide such as N-(2-dimethylaminoethyl) acrylamide and metacrylamide. They can be used in combination of two or more kinds. A used amount thereof is suitably in the range of 20 to 95 weight %, preferably 40 to 95 weight %.

The representative examples of the above water insoluble ethylenically unsaturated monomer (a-3) include unsaturated carboxylic acid esters such as metacrylic acid alkyl ester and maleic acid dialkyl ester;  $\alpha$ -olefins such as ethylene and propylene; aromatic vinyls such as styrene and  $\alpha$ -methylstyrene; vinyl esters such as vinyl acetate and vinyl propionate;

vinyl chloride; vinylidene chloride; and acrylonitrile. They can be used in combination of two or more kinds. A used amount thereof is suitably in the range of 0 to 75 weight %, preferably 0 to 50 weight %.

The representative examples of the above organic thiol compound (a-4) include alkylmercaptans such as n-octylmercaptan and n-dodecylmercaptan; aromatic mercaptans such as benzylmercaptan and dodecylbenzylmercaptan; thiocarboxylic acid or a salt thereof or alkyl esters thereof; and polythiols. These are used in the range of 0 to 40 weight %, preferably 0.2 to 30 weight %.

These organic thiol compounds (a-4) have the effects of stabilizing the polymerization in preparing the above aqueous copolymer and further allowing the following emulsion polymerization to be smoothly carried out. The use thereof exceeding the above range notably lowers the molecular weight of the aqueous copolymer.

The above various materials are reacted in water with a radical-forming catalyst. There can be used the compounds usually used as the catalyst therefor, such as water soluble peroxides including hydrogen peroxide, potassium persulfate and ammonium persulfate; organic peroxides such as cumene hydroperoxide and t-butyl peroxide; and azo series compounds such as azobisisobutyronitrile. Further, there can be applied a redox polymerization process in which these various compounds are used in combination with conventional various metal ions and reducing agents.

The reaction temperature and time can be selected from the ranges which are applied in a conventional

radical polymerization. Usually, they are 20 to 90°C and 15 minutes to 15 hours, respectively.

A pH value is usually adjusted in the range of 2 to 9.

Then, the aqueous copolymer thus obtained is used as the polymerizable emulsion dispersant for the emulsion polymerization of these ethylenically unsaturated monomers (a-1), (a-2) and (a-3) in the range of 0.5 to 50 weight parts, preferably 1 to 30 weight parts in terms of a solid matter content based on 100 weight parts of the mixture of 5 to 50 weight % of the above ethylenically unsaturated monomer (a-1), 95 to 50 weight % of the above ethylenically unsaturated monomer (a-3) and/or the above ethylenically unsaturated monomer (a-2).

A proportion of the the above ethylenically unsaturated monomer (a-1) used for preparing the polymer aqueous dispersion is suitably 5 to 50 weight %, preferably 5 to 30 weight %.

A proportion of the the above ethylenically unsaturated monomer (a-3) used for preparing the polymer aqueous dispersion (A) or a mixture of the monomers (a-1), (a-2) and (a-3) is suitably 95 to 50 weight %, preferably 95 to 70 weight % based on the whole ethylenically unsaturated monomers used for this emulsion polymerization.

As described above, the composition of the present invention can be prepared without using the conventional surface active agents. However, this does not remove the use of the aqueous polymer of the present invention in combination therewith.

The polymer aqueous dispersion (A) thus obtained has less foaming and an excellent mechanical and thermal stability in addition to a good storage stability.

Meanwhile, any compounds can be used as the above isocyanate series compound or polymer thereof (B) as long as they have two or more isocyanate groups in the molecules. There can be given as the particularly representative examples thereof, tolylenediisocyanate (TDI: "Dismodule T" as an example of a commercially available product, manufactured by Bayer Co., Ltd., Germany), hydrogenated TDI, a trimethylol propane - TDI adduct ("Dismodule L" as an example of a commercially available product), triphenylmethanetriisocyanate (TTI: "Dismodule R"), 4,4'-diphenylmethanediisocyanate (MDI: "Dismodule 44"), hydrogenated MDI, H<sub>2</sub>O - hexamethylene-diisocyanate addition condensation product ("Dismodule N"), xylenediisocyanate, and 4,4'-dicyclo-hexylmethane-diisocyanate.

Further, there can be used as well the component prepared by mixing polyols such as a hydroxy group-containing polyester or polyether with an excess of polyisocyanate, an NCO terminal prepolymer prepared by subjecting polyol and excessive polyisocyanate in advance to a prepolymerization, and the component prepared by adding polyisocyanate to an OH terminal prepolymer which is polymerized with excessive polyol.

The addition amount of the isocyanate series compound or polymer thereof (B) is preferably in the range of 1 to 200 % based on the solid matter weight of the polymer aqueous dispersion (A).

The composition can be obtained by using an aqueous copolymer without using a conventional surface active agent. While this aqueous polymer itself acts as a dispersant in preparing the polymer aqueous dispersion (A), the crosslinkable functional groups contained in the aqueous polymer contributes to the formation of a three-dimensional structure in using the composition of the present invention as a coating agent to allow them to be consumed as a film-forming component, so that the defects mentioned above are not generated.

Secondly, the polymer aqueous composition (A) contains both crosslinkable functional groups of the crosslinkable functional group component originating in the above aqueous polymer as the dispersant and the crosslinkable monomer component, and this allows the polymer aqueous dispersion (A) and the isocyanate series compound or polymer thereof (B) to react with all materials efficiently consumed and a minute three-dimensional network to be formed, whereby there can be obtained a lustrous and tough coated film having the excellent mechanical properties and sufficient hardness as well as the excellent anti-water, anti-corrosion anti-chemical and anti-solvent properties.

Thirdly, in a conventional aqueous paint, a base polymer requires a lot of a carboxylic group because of a water solubility thereof, which in turn requires a neutralizing step for neutralizing the carboxylic group with a lot of amines. In addition thereto, the polymer is dissolved in an aqueous solution containing a lot of a water soluble organic solvent in order to improve a solubility, which in turn results in the defects to

deteriorate the anti-alkali, anti-water, anti-corrosion and anti-weather performances.

In the present invention, a polymerizable aqueous dispersion contains less amount of the carboxylic group while containing no solvents in the volatile components. Accordingly, the composition of the present invention does not have such problem as the deterioration of the coated film performances due to the residual carboxylic groups.

The composition of the present invention is particularly suitable for a paint for metal but can be applied as well to the conventional uses for paper, fiber, concrete, plastics, wood, and others.

#### EXAMPLES

Next, the present invention will be explained below with reference to the examples. Part is expressed in terms of part by weight unless otherwise described.  
Preparation of the polymer aqueous dispersions (A)

An ethylenically unsaturated monomer, an organic thiol compound and water were put in a stainless steel reaction vessel as shown in Table 1. Further, potassium persulfate 4 parts was added to allow the mixture to react at 80°C for 30 minutes to thereby prepare an aqueous polymer. Then, the ethylenically unsaturated monomer mixture consisting of n-butyl acrylate 470 parts, styrene 400 parts,  $\beta$ -hydroxyethyl acrylate 100 parts and acrylic acid 20 parts was dropped thereto in the presence of the respective aqueous polymers at the same temperature over a period of 180 minutes for a polymerization and then pH was adjusted to 9, whereby

the polymer aqueous dispersions (A-1) to (A-3) were obtained.

For the sake of comparison, there were prepared the polymer aqueous dispersions (A'-1) and (A'-2) in which the monomer compositions constituting the above aqueous copolymers fell out of the scope of the present invention and (A'-3) which was prepared by an emulsion polymerization under the presence of a conventional surface active agent, whereby the polymer aqueous dispersions (A'-1) to (A'-3) for comparison were obtained.

Noigen EA 120 = PEG-Nonyl phenol ether  
Table 1

	A-1	A-2	A-3	A'-1	A'-2	A'-3
<u>Aqueous polymer</u>						
Surface active agent						
Emul O*1 = SDS	-	-	-	-	-	10
Noigen EA-170*2 = Poly ethyleneglycol - alkyl						-10 phenol ether
Monomer composition						
β-Hydroxyethyl acrylate	10	30	65	300	5	-
Acrylic acid	20	20	20	100	5	-
2-Ethylhexyl acrylate	5	-	-	150	40	-
Lauryl mercaptan	-	2	5	50	2	-
Deionized water		1500			1500	
Stability of polymer aqueous dispersion	A	A	A	B	C	A

\*1 Anionic surface active agent manufactured by  
Kao Soap Co.

\*2 Nonionic surface active agent manufactured  
by Daiichi Kogyo Seiyaku Co.

A: Excellent.

B: Increase in viscosity, which resulted in  
gelation.

C: Emulsion polymerization impossible.

#### Example 1 and Comparative Example 1

layer  
< 50 X  
A 50 % dimethylethanolamine solution 2 parts, ..  
Texanol 2 parts (a film forming aid manufactured by  
Eastman Kodack Co.) and Disperse Color SR-901 8 parts (a  
black coloring agent manufactured by Dainippon Ink &  
Chemical Ind. Co.) were added to the emulsions (A-1) and  
(A'-3) each 100 parts obtained above, respectively,  
while stirring well. Then, a 65 % ethyl acetate solution  
25 parts of Dismodule 44 (MDI manufactured by Bayer Co.,  
Germany) was added thereto and mixed well.

The paint thus prepared was sprayed on a soft plate  
subjected to a shot blast so that a dry thickness was 20  
 $\mu\text{m}$ , and was left for standing at a room temperature for  
3 days for drying.

Two test pieces thus obtained were subjected to an  
evaluation of the coated film performances and the  
results are shown in Table 2.

Table 2

	Example 1	Comp. Example 1
Pencil hardness	2H	F
Adhesion (cross cut)	100/100	60/100
Impact resistance (500 g)	50 cm OK	50 cm OK
Water resistance	No change after 240 hrs	Blister generated in 72 hrs
Salt Spray resistance	No change after 240 hrs Cellophane tape peel = 1 cm or less	Rust generated in 72 hrs

## Example 2 and Comp. Example 2

A 50 % dimethylethanolamine solution 2 parts, Texanol 3 parts, NS-200 50 parts (calcium carbonate manufactured by Nitto Hunka Co.) and Disperse Color SR-901 8 parts were added to the emulsions (A-2) and (A'-3) each 100 parts obtained above, respectively, while stirring well. Then, a 65 % ethyl acetate solution 35 parts of Dismodule 44 was added thereto and mixed well.

The paint thus prepared was sprayed on a soft plate subjected to a degrease with toluene so that a dry thickness was 100  $\mu$ m, and was forcibly dried at 80°C for 20 minutes and left for standing at a room temperature for 1 day.

Two test pieces thus obtained were subjected to the evaluation of the coated film performances and the results are shown in Table 3.

Table 3

	Example 2	Comp. Example 2
Pencil hardness	2H	H
Adhesion (cross cut)	100/100	80/100
Impact resistance (500 g)	50 cm OK	50 cm OK
Water resistance	No change after 30 days	Blister generated after 2 days
Salt Spray resistance	No change after 500 hrs	Rust generated in 72 hrs

#### Example 3 and Comp. Example 3

A 50 % dimethylethanolamine solution 2 parts, Texanol 3 parts, red iron oxide 75 parts and zinc white 25 parts were added to the emulsions (A-3) and (A'-3) each 100 parts obtained above, respectively, while stirring well. Further, a 65 % ethyl acetate solution 25 parts of Dismodule 44 was added thereto and mixed well.

The subbing paint thus prepared was coated with a brush on a soft plate subjected to a degrease with toluene so that a coated amount was 150 g/m<sup>2</sup>, and was left for standing at a room temperature for one night for drying, whereby two coated test pieces were prepared.

Meanwhile, a 50 % dimethylethanolamine solution 2 parts, Texanol 3 parts and Taibake R-930 35 parts (rutile type titanium oxide manufactured by Ishiwara Sangyo Co.) were added to the emulsion (A-1) 100 parts while stirring well. Then, a 65 % ethyl acetate solution 25 parts of Dismodule 44 was added thereto and mixed well.

The overcoating paint thus prepared was coated with a brush on the above subbed plate so that a coated amount was 130 g/m<sup>2</sup>, and was left for standing at a room temperature for 3 days for drying.

Two test pieces thus obtained were subjected to the evaluation of the coated film performances and the results are shown in Table 4.

Table 4

	Example 3	Comp. Example 3
Pencil hardness	2H	H
Adhesion (cross cut)	100/100	80/100
Impact rresistance (500 g)	50 cm OK	40 cm OK
Water resistance	No change after 30 days	Blister generated after 10 days
Salt Spray resistance	No change after 500 hrs	Rust generated in 500 hrs